Influence of Ionic Interaction on the Properties of Phosphors: Controlling the Luminescence Properties and Enhancing the Stability against Heat and Moisture

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要約

Worldwide, electric lighting consumed about 19% electricity of total global electricity consumption. It is widely accepted that white light emitting diodes (W-LEDs) will take the place of traditional ones like incandescent and fluorescent lamps because the environmentally friendly, energy efficient, long life time and compactness features. The invention of brightness InGaN blue LEDs by Isamu Akasaki, Hiroshi Amano and Shuji Nakamura has led to the realization of devices capable to produce white light efficient with phosphors. Light emitting diodes have attracted great research interest due to the lower energy consumption and longer operation time than the traditional devices. Phosphors play important roles in light emitting diodes the light output intensity is determined by the semi-conductor chips and phosphors. The inorganic phosphors play important roles in all the above approaches. Normally, inorganic phosphors are crystalline hosts doped with a small amount of activators which can be rare earth or transition metal ions. The atomic scale structure is relevant to the properties of the phosphors. In this work, the relationship between the properties of phosphors and the crystal structure is focused.

It is widely accepted that the properties of luminescence centers are affected by the nehelauxetic effect and crystal field splitting. The emission strength in red region is still insufficient. The maximal excitation wavelength of $(Ba,Sr)_2SiO_4:Eu^{2+}$ phosphor falls in the range of 390–400 nm, which is not an appropriate characteristic for the combination with blue LED chips (440–460 nm). The preliminary research has revealed that $Sr_2SiO_4:Eu^{2+}$ exhibits interesting orange emission when activated with a large amount of Eu^{2+} ions. However, the red shift of Eu^{2+} with increasing concentration of Eu^{2+} in Sr_2SiO_4 cannot be explained by the nehelauxetic effect and crystal field splitting. Here the $(Ba,Sr)_2SiO_4:Eu^{2+}$ phosphors are synthesized by a liquid phase precursor method. The DFT calculation and Rietveld refinement of X-ray diffraction patterns indicate that Eu ions prefer to occupy the 9 fold coordinate sites than the 10 fold ones. The density of states implies that the neighboring Eu ion may reduce the energy difference of *f* and *d* orbitals. In phosphors with high concentration of luminescence center, it is more likely to form neighboring Eu-Eu groups, leading to

lower the energies of *f-d* and *d-f* transitions and red shift. By this mechanism, high efficiency orange phosphors are realized when the concentration of Eu^{2+} is ≥ 25%.

Ce^{4+}-based luminescence materials are rare. The luminescence phenomenon is ascribed to the O^{2-}-Ce^{4+} charge transfer. Up till now, only Sr_2CeO_4 has been discovered as phosphor but the excitation wavelength (250-400 nm, peak: ~290 nm) is too short for LEDs application. The high excitation energy is due to the short Ce-O bonds. A series of new Ce^{4+}-based phosphors $Sr_{4.4}Ce_{2.6}REZnO_{12}$ (RE = Y, La, Eu) are discovered. The $Sr_{4.4}Ce_{2.6}REZnO_{12}$ (RE = Y, La, Eu) phosphors can be excited by a much longer wavelength (250-450 nm, peak: ~365 nm). The long wavelength excitable property is originated from the extremely long Ce-O bonds. The extremely long bond length of Ce-O is due to the stretching effect of $[ZnO_3]$ units. The O3 ions bond with Zn and Ce ions. The relatively strong covalent Zn-O bond attract the O3 ions from Ce ions. The La series gave more intense emission than Y series overall which is further confirmed by the higher internal quantum efficiency of RE=$Eu_{0.75}La_{0.25}$ (42.2%) than RE=$Eu_{0.75}Y_{0.25}$ (33.8%). The temperature dependence of the relative integrated photoluminescence intensities also demonstrated that RE=$Eu_{0.75}La_{0.25}$ had a better performance than RE=$Eu_{0.75}Y_{0.25}$ against thermal quenching. This phenomenon is explained by the electron density and stable/meta-stable site distribution of Zn^{2+}. The experimental three-dimensional electron density calculated by the maximum-entropy method demonstrates that the high charge density positions correspond to the atom sites. The charge density distributes broadly along the [001] direction corresponding to the Zn1 and Zn2 sites due to the thermal vibration of Zn in c-axis. The Zn1 and Zn2 configurations are con-sistent with the single crystal diffraction analysis result. The Zn1 and Zn2 sites are stable and meta-stable, respectively, because the Zn1 site is in the equilibrium position when the Zn ion swings in sequence of Zn2-Zn1-Zn2. The charge density in (010) plane indicates that more Zn ions are distributed in the Zn2 sites for Y sample compared to the Eu and La ones, which is in line with the site occupancy. Therefore, the statistical domination of meta-stable Zn2 configuration in the Y series gives a raise to lattice vibration, resulting in a poor luminescence performance compared to La series.

The combination of a near-ultraviolet (n-UV) LED (350–420 nm) with a single-phase full colour-emitting phosphor is an alternative way to generate warm white light. White light emission is achieved by the combination of blue Ce^{3+}, green Tb^{3+} and red Mn^{2+} in $Ca_3Y(AlO)_3(BO_3)_4$ and $Ca_3Gd(AlO)_3(BO_3)_4$ hosts. It is discovered that large ions (Ca^{2+}, Ce^{3+}) are more likely to occupy the smaller sites while small ions (Mn^{2+}, Y^{3+}, Gd^{3+}) occupy the larger sites. The anomalous site occupancy behavior is due to some extremely short bonds in the large sites: The bucket effect inhibits the occupancy of large size ions. The major reason for Ce^{3+} emission broadening is the cation disorder in the metal ion framework, while anion disorder is the minor

one. White light emission with desirable IQEs of 54% and 43% for CYAB:5%Ce^{3+},20%Tb^{3+},2%Mn^{2+} and CGAB:5%Ce^{3+},20%Tb^{3+},2%Mn^{2+} was realized by adjusting the Ce^{3+}, Tb^{3+} and Mn^{2+} emission and energy transfer. The luminescence chromaticity shifts slightly as the temperature increases, which is due to the sharper thermal quenching of Mn^{2+} than Ce^{3+} and Tb^{3+} ions. It is expected that the chromaticity shifts are improved by increasing the content of Mn^{2+} ions and/or homogeneous distribution of activators.

Stability is crucial for functional materials. Many high efficient luminescence materials suffer from chemical degradation due to moisture. To investigate the key factor of the stability against moisture, the $(Ba,Sr)_3SiO_5:Eu^{2+}$ analogues are ideal models because the stability of $(Ba,Sr)_3SiO_5:Eu^{2+}$ vary according to the ratio of Ba/Sr. The anion size is one of the factor affecting the stability against moisture of materials. The lower stability of Ba-rich samples is originated from the dispersive electrons of O^{2-}. The large volume of electron cloud for large anion increases the possibility of electron losing and effective collision. Therefore, materials containing large size anions tend to be more reactive: It is well known that phosphides and sulfides are unstable compared to nitrides and oxides. Nevertheless, this law cannot explain the remarkable stability difference among materials sharing the same anion. When the concentration of Sr increases, the local space of O^{2-} becomes smaller, the electron cloud of O^{2-} shrinks accordingly. The less dispersive electrons resulted in lower possibility of effective collision and reactivity. The electron dispersion is shaped by the space which can be described by VDP. The moisture resistance enhanced when the VDP became smaller. Thus, VDP is suggested to be an indicator to evaluate the electron cloud size and the moisture resistance. The thermodynamic instability and lattice vibration potential can be measured by GII, indicating the relationship between GII and thermal quenching. The temperature dependent emission intensities and Rietveld refinement supported the negative correlation of GII and thermal resistance. Concepts of VDP and GII are extendable to other host lattices. The results provide insights and criteria to design new phosphors with high chemical stability and thermal resistance.

Stability of material is one of the most important features pursed by researchers. Most Eu^{2+}-doped luminescence materials are unstable in high temperature (≥ 600 °C) due to thermal oxidization of Eu^{2+} into Eu^{3+}. It is discovered that $SrLuAl_2Si_2O_2N_5:Eu^{2+},Ce^{3+}$ phosphors are very stable even though treated in 800 °C for 2 hours in air. The $SrLuAl_2Si_2O_2N_5$ host contains the $[N(Al/Si)_4]$ units. Such units are rare because one nitrogen bonds with one to three Al/Si generally. The high stability of $SrLuAl_2Si_2O_2N_5$ is originated from this feature. On one hand, the high connectivity of $SrLuAl_2Si_2O_2N_5$ framework is responsible for the host stability. On the other hand, the N^{3-} ions in the host lattice sacrifice instead of Eu^{2+}, protecting Eu^{2+} from oxidization.

Several approaches are available to develop new phosphors. The first is using old phosphors systems but

new to LED application. However, the existed old phosphors have been highly developed. Therefore, other alternative approaches should be considered. The second one is develop new phosphors from solid solutions. The properties of phosphors can be further optimized by tuning the composition of solid solutions. For instance, the stiffness of the host lattice may be enhanced by using elements of low electronegativity. The third one is to develop phosphors from known materials which are never doped with luminescence centers. Certainly, this approach has been proved to be effective. Nevertheless, the known materials are not infinite. Therefore, the fourth method was put forward to make entirely novel structure. A completely new material that would need to hurdle the arduous task of determining the right structure is undeniably an effective strategy.

In the future, the existing uses and emerging frontiers justify the resources utilized toward the continuous. For instance, red phosphors may be applied in light conversion films or LED plant lamp. The emission at 400-470 nm and > 600 nm corresponds to the range of useful wavelength for plants. Thus, NUV or green light excitable red materials are ideal candidates for this application.